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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


REC'D 15 JUN 2004

WIPO PCT

Applicant's or agent's file reference 9484	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/GB 02/05761	International filing date (day/month/year) 18.12.2002	Priority date (day/month/year) 22.01.2002
International Patent Classification (IPC) or both national classification and IPC B01J37/02, B01J37/02		
Applicant BP CHEMICALS LIMITED		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 11 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☒ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  12.08.2003	Date of completion of this report  15.06.2004
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**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-11 as originally filed

**Claims, Pages**

12, 13 as originally filed

14-16 received on 11.05.2004 with letter of 06.05.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

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**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees, the applicant has:

- ☐ restricted the claims.
- ☒ paid additional fees.
- ☒ paid additional fees under protest.
- ☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- ☐ complied with.
- ☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- ☒ all parts.
- ☐ the parts relating to claims Nos. .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-37
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-37
Industrial applicability (IA)	Yes: Claims	1-37
	No: Claims	

2. Citations and explanations

**see separate sheet**

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**Re Item IV**

**Lack of unity of invention**

1. The International Examining Authority agrees with the objection put forward by the International Search Authority as to lack of unity within the meaning of Rule 13.1 PCT.

2. The separate (groups of) inventions are:

1st invention, claims 1-14:

A process for preparing a catalyst active for the fluid bed acetoxylation of ethylene to produce vinyl acetate.

2nd invention, claims 15-28:

A process for impregnating microspheroidal catalyst support particles with at least one compound of a catalytically active group VIII noble metal.

3rd invention, claims 29-32:

A process for the purification of a waste stream comprising dilute aqueous hydrazine.

4th invention, claims 33-37:

A process for impregnating porous microspheroidal particles with one or more salts of group I, group II, lanthanide and transition metals.

3. The reasoning for lack of unity as detailed in the International Search Report remains valid, the reasoning being as following:

There are four (4) independent claims:

Claim 1: a process for preparing a catalyst active for the fluid bed acetoxylation of ethylene to produce vinyl acetate

Claim 15: a process for impregnating microspheroidal catalyst support particles

Claim 29: a process for the purification of a waste stream comprising dilute aqueous hydrazine

Claim 33: a process for impregnating porous microspheroidal particles

It appears that within these independent claims unity does not exist for the following reasons:

- A1) The "same" or "corresponding" technical feature between these 4 independent claims is a (catalytically active) component on a support.

This feature is already known from GB-A-1314225 (see example 1) and GB-A-1266623 (see example 2), where Pd and Au are supported on a spheroidal silicic acid carrier.

Therefore, this feature is not a special (new and inventive) technical feature. Thus, no "same" or "corresponding" special technical features could be found between the independent claims 1, 15, 29 and 33, as required by Rule 13.2 PCT.

- A2) The "same" or "corresponding" technical feature between the independent claims 1, 15 and 33 is a process for impregnating microspheroidal particles with at least one compound.

This feature is already known from GB-A-1266623 (see example 2) and EP-A-672453 (see example 2), where Pd and Au are impregnated on a microspheroidal silicic acid carrier, and whereby said carrier is mixed and thoroughly kneaded with a quantity of an aqueous solution containing Pd and Au, which is just sufficient to permit absorption thereof by the silicic acid carrier.

The term microspheroidal used in the present application can be clarified using the passage mentioned on page 3, lines 9 to 24 of the specification, where is disclosed that at least 80% and preferably at least 90% of the support particles have mean diameters of less than about **300 microns**.

Document GB 1 266 623 discloses that the support particles have a diameter from 0.1 mm (i.e. 100 microns) to 1.5 mm (1500 microns). In example 2, the support particles used have a size between 0.1 and 0.2 mm, i.e. range from **100 to 200 microns**. The supported catalyst is used in **fluidized bed** acetoxylation of ethylene to produce vinyl acetate.

For the sake of completeness, it is noted that it is the aim of the present invention

to provide an improved process for the commercial scale preparation of a catalyst active for the fluid bed acetoxylation of ethylene to produce vinyl acetate (see page 1, lines 19-21 of the specification). Since both the present invention and the prior art mentioned above are concerned with fluid bed reactions, both the catalyst of GB 1 266 623 and the one of the present invention must be of the same order of magnitude.

Therefore, this feature is not a special (new and inventive) technical feature. Thus, no "same" or "corresponding" special technical features could be found between the independent claims 1, 15 and 33, as required by Rule 13.2 PCT.

- A3) The "same" or corresponding technical feature between the independent claims 1 and 15 is a process for preparing a catalyst by impregnating a microspheroidal catalyst support particle by incipient wetness technique whilst agitating the support and drying the impregnated support particles whilst agitating.

This feature is already known from GB-A-1266623 (see example 2), where Pd and Au are supported on a microspheroidal silicic acid carrier by impregnation with a solution containing a quantity of water just sufficient to permit absorption thereof by the carrier, whilst kneading and mixing. Subsequently the mixture was dried in a glass tower by injection of nitrogen.

Therefore, this feature is not a special (new and inventive) technical feature. Thus, no "same" or "corresponding" special technical features could be found between the independent claims 1 and 15, as required by Rule 13.2 PCT.

- A4) As "same" or corresponding technical feature between the independent claims 1 and 29, between the independent claims 15 and 29, and between the independent claims 29 and 33 only the same as under point A1) above could be found.

No other "same" or "corresponding" special technical features could be found between the independent claims 1 and 29, between the independent claims 15 and 29, and between the independent claims 29 and 33, as required by Rule 13.2 PCT.

- B1) The problem underlying claim 1 can be seen as to provide a further process for preparing a catalyst active for the fluid bed acetoxylation of ethylene to produce vinyl acetate.

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The problem underlying claim 15 can be seen as to provide a further process for impregnating microspheroidal support particles with at least one compound of a catalytically active group VIII noble metal by the incipient wetness technique.

The problem underlying claim 29 can be seen as to provide a further process for the purification of a dilute aqueous hydrazine comprising waste stream.

The problem underlying claim 33 can be seen as to provide a further process for impregnating porous microspheroidal particles with one or more salts, whereby the solvent is contained within the pore volume of the support particle.

Thus, the problems are not the same and there is no common problem which could serve as the general inventive concept required by Rule 13.1 PCT.

- B2) Furthermore, the problem to provide a process for impregnating microspheroidal particles with compounds by the incipient wetness technique is known from GB-A-1266623 (see example 2), where a silicic acid catalyst carrier is mixed and thoroughly kneaded with a quantity of an aqueous solution containing Pd and Au, which is just sufficient to permit absorption thereof by the silicic acid carrier.

No other common problem could be found which could serve as the general inventive concept required by Rule 13.1 PCT.

Consequently, these claims are not unitary according to Rule 13 PCT.

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: GB-A-1 314 225 (KNAPSACK AG) 18 April 1973 (1973-04-18)
- D2: GB-A-1 266 623 (KNAPSACK AG) 15 March 1972 (1972-03-15)
- D3: GB-A-1 250 265 (KNAPSACK AG) 20 October 1971 (1971-10-20)
- D4: EP-A-0 672 453 (STANDARD OIL CO OHIO) 20 September 1995 (1995-09-20)  
cited in the application
- D5: DE 31 19 707 A (KRAFTWERK UNION AG) 2 December 1982 (1982-12-02)

D6: US-A-4 801 573 (RIIS TRYGVE ET AL) 31 January 1989 (1989-01-31)

**I) First invention** (claims 1-14)

1. Documents D2 (page 2, lines 8-63; example 2) and D4 (page 4, line 42 to page 6, line 1; example 2) disclose a process for impregnating a microspheroidal  $\text{SiO}_2$  support with palladium and gold via the incipient wetness technique, while thoroughly kneading and mixing the carrier with the impregnation solution. After reduction of the noble metals, the catalyst mass was washed and kneaded with a concentrated solution of potassium acetate in water, followed by drying.

The subject-matter of independent claim 1 differs from D2 and D4 in that in the catalyst preparation of D2 and D4 aqueous solutions of potassium acetate are used, whereas in claim 1 the reduced and washed catalyst cake is blended with solid salts of one or more Group I, Group II lanthanide and transition metals.

To the applicant is pointed out that currently there is no evidence on file to support any unexpected effects or properties in relation to this difference. Alleged but unsupported advantages cannot be taken into consideration in respect of the determination of the problem underlying the application.

The problem underlying the invention can be formulated as to provide a further process for preparing a microspheroidal vinyl acetate catalyst.

Depositing metal compounds via blending metal salts with a wet support is a method known by the skilled person (see D6, column 4, lines 50-53).

Therefore, no inventive step can be recognised for the subject-matter of independent claim 1. It does not fulfill the requirement of Article 33(3) PCT.

2. Dependent claims 2-14 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, involve an inventive step with respect to the prior art named in the present proceedings.

The reasons therefor are that the additional features of the said claims either are directly known from documents D1-D4 and D6, or is a combination of features obvious to the man skilled in the art in consideration of the disclosure of the prior



art named in the present proceedings, or they concern modifications which lie within the normal practice of the man skilled in the art.

**II) Second invention** (claims 15-28)

1. None of the cited documents explicitly mention to carry out steps (a') and (b') in one apparatus. The subject-matter of independent claim 15 is therefore novel (Article 33(2) PCT).

Performing steps (a') and (b') in the same apparatus enables a reduction in catalyst handling to be achieved.

Taking either document D1 or D2 as closest prior art, the objective problem underlying the invention can be seen as to provide a further process for impregnating microspheroidal catalyst support particles with at least one group VIII noble metal compound, which allows a reduced catalyst handling.

The solution to the above formulated problem provided for in independent claim 15 is obvious for the skilled person in light of the available prior art. Neither D1 nor D2 teach that it would not be possible to carry out both steps in a single vessel, thus documents D1 nor D2 teach away from the present invention, contrary to the suggestion of the applicant; D1 is silent about the use of a second vessel for the drying step (see example 1), there is no general teaching in D2 to use separate vessels (in example two vessels are used).

2. Dependent claims 16-28 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, involve an inventive step with respect to the prior art named in the present proceedings (Article 33(3) PCT).

The reasons therefor are that the additional features of the said claims are either a combination of features obvious to the man skilled in the art in consideration of the disclosure of the prior art named in the present proceedings (D1-D4 and D6), or they concern modifications which lie within the normal practice of the man skilled in the art.

**III) Third invention** (claims 29-32)

1. Document D5 is regarded as being the closest prior art to the subject-matter of claim 29, and discloses that **it is known** (at least since 18.05.1981) **to decompose hydrazine**, which is present in hydrazine containing water, **with catalysts, such as ruthenium or palladium** (see page 2, lines 18-23). **Curve 4 represents the hydrazine decomposition rate of a ruthenium catalyst** (see page 5, lines 8-11); the Y-axis represents the hydrazine concentration of an aqueous hydrazine solution in ppm (see page 4, lines 17-21). The ruthenium catalyst shows the best hydrazine decomposition rate.

D5 does not explicitly disclose that the catalyst comprises ruthenium on support. Hence, formal novelty can be accepted for the subject-matter of claims 29-32 (Article 33(2) PCT).

The argument of the applicant that D5 directs the skilled man away from the use of ruthenium as a catalyst due to the expense of the metal is not convincing; the merit of D5 is that it shows that ruthenium and palladium catalysts have been **commonly** used before 1981 to decompose hydrazine. D5 provides an alternative catalyst.

Thus, no inventive step can be recognised for the subject-matter of claims 29-32 (Article 33(3) PCT). Supporting ruthenium is one of the straightforward possibilities the skilled person would select from in order to provide a process for decomposing hydrazine in the presence of a further ruthenium catalyst.

**IV) Fourth invention** (claims 33-37)

1. It has not been established that the problem as described on page 1, lines 18-21 of the application is solved by the process as defined in independent claim 33. The presence of Group VIII noble metals and an optional promoter selected from gold, copper and cerium is required to arrive at useful vinyl acetate catalysts.

Accordingly, an inventive step cannot be recognised for the subject-matter of claims 33-37 (Article 33(3) PCT).

2. Document D6 discloses that the method of depositing active metals on (alumina)

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support, whereby metal salts are mixed with the wet support in a suitable blender to obtain a substantially homogeneous mixture, is one of the various methods well known to those skilled in the art (see column 4, lines 40-53).

The argument of the applicant that D6 does not teach the use of solid salts, nor blending solid salts with a support which has solvent contained within its pore volume is not convincing: metal salts are normally solid; a wet support has at least some solvent (e.g. water) within its pores.

Therefore, no inventive step can be recognised for the subject-matter of claims 33-37 in view of D6 (Article 33(3) PCT).

**Certain defects in/observations on the international application**

1. To meet the requirements of Rule 5.1(a)(ii) PCT, documents D1-D3, D5 and D6 should be identified in the description and the relevant background art disclosed therein should be briefly discussed.

catalyst containing at least about 0.1wt% to about 5wt% palladium and about 0.1 to about 3wt% gold. EPO - DG 1

15. A process for impregnating microspheroidal catalyst support particles with at least one compound of a catalytically active group VIII noble metal, which process comprises the steps of:

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(a') impregnating the microspheroidal support particles by the incipient wetness technique with an aqueous solution of the at least one catalytically active group VIII noble metal, whilst agitating the support particles; and

(b') drying the impregnated support particles produced in step (a') whilst agitating the impregnated support particles;

wherein steps (a') and (b') are performed in the same apparatus, said apparatus comprising an agitated blender.

16. A process according to claim 15 in which step (b') comprises agitating the impregnated support particles whilst applying external heat at a temperature in the range 50 to 200°C.

17. A process according to claim 15 or claim 16 in which the microspheroidal support particles are selected from the group consisting of silica, alumina, zirconia and mixtures thereof.

~~18. A process according to any one of claims 15 to 17 in which step (a') and step (b') are performed in the same apparatus, said apparatus comprising an agitated blender.~~

~~19.~~ 18. A process according to any one of claims 15 to ~~18~~ 17 in which the at least one catalytically active group VIII noble metal comprises palladium.

~~20.~~ 19. A process according to any one of claims 15 to ~~19~~ 18, further comprising a step (c'), which comprises, contacting the impregnated support particles with a reducing agent to convert the at least one compound to its respective metal.

~~21.~~ 20. A process according to claim ~~20~~ 19 wherein the impregnated support particles are added to a solution of a reducing agent active for reduction of the at least one metal compound to its respective metal whilst stirring.

~~22.~~ 21. A process according to claim ~~20~~ 19 or claim ~~21~~ 20 wherein the reducing agent comprises an aqueous solution of hydrazine.

~~23.~~ 22. A process according to claim ~~22~~ 21 wherein the concentration of hydrazine in the aqueous solution is 1 to 20 wt%.

~~24.23.~~ A process according to claim ~~2322~~ wherein the concentration of hydrazine is 3 to 20 wt%.

~~25.24.~~ A process according to any one of claims ~~2221~~ to ~~2423~~ in which the at least one compound of a catalytically active metal impregnated in the support comprises  
5 palladium and gold compounds.

~~26.25.~~ A process according to any one of claims 1 to 14 and 12 to ~~2524~~ in which unreacted hydrazine washed from the material after the reduction step is decomposed in the absence of an oxidant over a supported ruthenium catalyst to nitrogen and ammonia.

~~27.26.~~ A process according to any one of claims ~~2019~~ to ~~2625~~, further comprising a  
10 step (d') wherein the support particles are further impregnated with one or more salts of Group I, Group II, lanthanide and transition metals, by blending the particles with one or more solid salts of Group I, Group II, lanthanide and transition metals in the presence of a solvent for the salt in which the solvent is contained within the pore volume of the catalyst support particle.

~~28.27.~~ A process according to claim ~~2726~~ wherein the solvent is water.

~~29.28.~~ A process according to claim ~~2726~~ or claim ~~2827~~ which further comprises a step (e') wherein the impregnated particles are dried at a temperature in the range from 60°C to 150°C.

~~30.29.~~ A process for the purification of a waste stream comprising dilute aqueous  
20 hydrazine, which process comprises contacting the waste stream with a catalyst active for the decomposition of the hydrazine to nitrogen and ammonia; said catalyst comprising ruthenium on a support.

~~31.30.~~ A process according to claim ~~3029~~ in which the amount of ruthenium on the support is in the range from 1 to 10 % by weight.

~~32.31.~~ A process according to claim ~~3029~~ or claim ~~3130~~, wherein the support is an  
25 inorganic oxide, activated carbon or graphite.

~~33.32.~~ A process according to claim ~~3231~~ wherein the inorganic oxide is selected from the group consisting of silica, alumina, zirconia and mixtures thereof.

~~34.33.~~ A process for impregnating porous microspheroidal particles with one or more  
30 salts of Group I, Group II, lanthanide and transition metals which process comprises blending the particles with one or more solid salts of Group I, Group II, lanthanide and transition metals in the presence of a solvent for the salt in which the solvent is contained within the pore volume of the support particle.

~~35.34.~~ A process according to claim 3433 wherein the solvent is water.

~~36.35.~~ A process according to claim 3433 or claim 3534, which further comprises the step of drying the impregnated particles at a temperature in the range from 60°C to 150°C.

5    ~~37.36.~~ A process according to any one of claims 3433 to 3635 wherein the blending is performed in a blender.

~~38.37.~~ A process according to any one of claims 3433 to 3736 in which the microspheroidal support particles are selected from the group consisting of silica, alumina, zirconia and mixtures thereof.

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